

CHROMATOGRAPHIC DETECTORS FOR ANALYSIS OF GASES AND VAPORS
OF ORGANIC SUBSTANCES IN THE ATMOSPHERES OF THE EARTH AND PLANETS

V. V. Brazhnikov and V. A. Rotin

Translation of: "Khromatograficheskiye detektory dlya analiza gazov
parov organicheskikh veshchestv v atmosferakh zemli i planet,"
Institute of Space Research, USSR Academy of Sciences, Moscow,
Report Pr-100, 1972, 48 pp.

(NASA-TT-F-14598) CHROMATOGRAPHIC
DETECTORS FOR ANALYSIS OF GASES AND VAPORS
OF ORGANIC SUBSTANCES IN THE ATMOSPHERES OF
THE EARTH AND PLANETS V.V. Brazhnikov, et
al (NASA) Oct. 1972 34 p CSCL 14B

N72-33385

Unclas
44613

CSCL 14B G3/14



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 OCTOBER 1972

CHROMATOGRAPHIC DETECTORS FOR ANALYSIS OF GASES AND VAPORS OF ORGANIC SUBSTANCES IN THE ATMOSPHERES OF THE EARTH AND PLANETS

V. V. Brazhnikov and V. A. Rotin

ABSTRACT. The article deals with practical and currently used gas detectors. Primary emphasis is placed on adapting such detectors for use in spacecraft and for use in unmanned probes. Each type of detector is discussed and its advantages and limitations are set forth.

The method of gas chromatography has begun to acquire great significance /1*
for the analysis of the components of gases in the cabins of spacecraft [1],
and for investigating the atmosphere of the Earth and other planets of the
Solar System [2-4].

However, although at the present time methods of separating gaseous
organic and inorganic compounds are developed to a sufficient extent and
several surveys have been published on this question [5-7], methods of highly
sensitive gas analysis have not been sufficiently developed.

The task of this work is the investigation of certain types of chromatographic detectors with the goal of utilizing them and automatic space chromatographs for the analysis of gaseous substances in the atmosphere of planets of the Solar System.

At present, for analysis of gases, the following types of detectors can be used [8,9].

* Numbers in margin indicate pagination in foreign text.

I. Thermoconductivity Detector (TCD).

Thermoconductivity detectors (katharometers) of varied design are widely used in gas chromatography. A description of the principles of operation and design of TCD can be found in a majority of the textbooks on gas chromatography [8, 10-12]. Many articles and surveys on chromatographic detectors also contain chapters on TCD [13-16]. Therefore, only a few characteristics of employing TCD for gas analysis will be examined.

Since TCD measures the difference in thermoconductivity between the carrier gas and the mixture of substances distributed in the carrier gas, for achieving the highest sensitivity it is necessary that the carrier gas and the analyzed substance be strongly differentiated with respect to thermoconductivity. Consequently, for analyzing gases with a low thermoconductivity one must use a carrier gas with a high thermoconductivity (H_2 , He), and vice versa.

At any rate, two possible methods of obtaining peaks on the TCD exist:

(1) There is a maximum or a minimum proportionate to thermoconductivity and the content of the binary mixture (the carrier gas and the analyzed gas). For example, a number of studies were conducted [17-20] pertaining to the study of anomalous behavior of H_2 during its gas chromatographic analysis in a TCD using He in the capacity of a carrier gas. Readings for H_2 and He must be positive; however, inverse hydrogen peaks have been observed with the formation of an M-shaped peak which was explained by the presence of a minimum of thermoconductivity of the mixture with a composition of 8% H_2 and 92% He [17]. For eliminating the inversion it was suggested to employ for the analysis of H_2 and He a mixture of 8.5% H_2 with He in the capacity of a carrier gas [18].

(2) Thermoconductivity is not critical during calculation of heat loss from the heated filament of a TCD [21].

In case N_2 , Ar or CO_2 is used in the capacity of a carrier gas, having low thermoconductivity (heat), near the temperature of the analyzed substance, a significant effect will be manifested by their thermal capacities. Here both positive and negative peaks are possible which increase proportionate to the increase in the flow rate of the carrier gas; inversion peaks are also possible [18].

The behavior of anomalous peaks depends on the temperature of the sensitive elements (bridge current), and the nature and flow rate of the carrier gas, as well as the size of the sample [22]. Therefore, use of N_2 , Ar and other carrier gases is not recommended if the limits of anomalous behavior of the gases under analysis have not been established [23].

A study has been conducted pertaining to the use of binary gaseous mixtures in the capacity of carrier gases. For example, CO_2 was analyzed in a carrier gas consisting of 70% N_2 and 30% He [24]. /5

A slight increase in the sensitivity of the TCD was obtained by means of using it at decreased pressure, if the working conditions were constantly maintained [25]. However, since the thermoconductivity decreased proportionate to the decrease in pressure, the TCD could not be used at pressures lower than 25 mm Hg. Use of decreased temperatures for the work regime of the TCD allowed an increase in the sensitivity of the detector to constant gases [26].

Use of the TCD during the analysis of inert gases has been described in a number of studies both with the use of carrier gases with a high thermoconductivity (He, H_2) [27-28], as well as with gases with a low thermoconductivity (N_2 , Ar) [29-30]. A method of analyzing organic compounds has also been employed by means of converting the substance to be analyzed in catalyzers to CO_2 , H_2 , or CH_4 with subsequent analysis of the obtained gases [12, 31].

For prospective analysis of inert gases and vapors of volatile substances in the atmosphere of Mars [4] a special micro-detector for thermoconductivity was built. The sensitive element of the detector is made from Pt-Ro wire with a diameter of 0.5 microns and a length of 0.3 mm and has a resistance of nearly 400 ohms; this micro-detector operates on a total bridge current of 3.5 microamperes. As a result of the small size and small working volume (1 μA) the low power requirements (5 mW) and high sensitivity (5 ppm) similar detectors can be widely used for all compounds with respect to space goals, especially in the event micro-precipitation and capillary columns are used with a flow rate less than 1 ml/min.

The basic characteristics of a thermoconductivity detector are presented in Tables 1 and 2.

2. Thermistor Detector (Ther D.).

The thermistor detector is a variation of detectors for thermal conductivity, since it has the ability to change electrical resistance with a change in temperature [8]. The sensitive element of this type of detector is a sphere with a diameter of nearly 0.5 mm made from a sintered mass of oxides of Mn, Co and Ni with additives for obtaining the necessary electrical characteristics. The spheres are enclosed in a glass envelope, in order to make them inert with respect to the surrounding medium.

Thermistor spheres have a high negative temperature coefficient of resistance. Therefore, at low temperatures it is possible to obtain higher sensitivity than is the case when using TCD. This property of thermistors is especially important for an analysis of gases at low temperatures.

It is necessary to take into account that the dependence of thermistor readings on bridge current occurs through a maximum, that is, an optimal current value for the thermistor exists which it is necessary to employ.

Generally, maximum sensitivity is observed with a bridge current of from 10 to 15 μ A. It is also necessary to take into account that the glass covering of thermistors can be broken. In this case, when using hydrogen as a carrier gas, oxides can be reduced. As a result of the small size of the sphere, the thermistors can be used with capillary and micro-precipitation columns, for example, for an analysis of oxygen isotopes or hydrogen isotopes in glass, adsorption capillary columns [32]. However, it is necessary to take into account that the time constant of the thermistor (1-10 seconds) is higher than that of the katharometer, and that its linearity is significantly less. Generally, the use of the thermistor detector in place of the katharometer is not recommended except in certain special cases [33-34]. The basic characteristics of the thermistor detector are presented in Table 1.

3. Density Detection (DD).

Density detection was first described by Martin [35]. However, the detector was so complex in design that notwithstanding slight simplification [36] it was not very widely employed [46]. Recently, a more simply designed density

NASA

detector has been suggested [38, 39]. The sensitive elements of the detector can be spirals, as in the thermistor, and in this case sensitivity of such detectors differs insignificantly and is equal to $8-20 \cdot 10^{-6}$ mg/ml for butane [40].

A description of the operating principles of the density detector can be found in a number of published works [38, 41, 42].

With an increase in pressure in the detector, the difference in density increases and the sensitivity of the detector increases. The sensitivity of the density detector decreases proportionately to an increase in temperature.

Selection of a carrier gas for the density detector has great significance [43]. The best carrier gases, as was shown by Martin and James [44], are gases with a low thermoconductivity and a high thermal capacity, so that the detector would be more sensitive to changes in current. Therefore, for obtaining the high sensitivity, the use of He and H_2 is not recommended, however, with the use of such gases of Hg, N_2 and CO_2 , the sensitivity of the detector is made worse than the sensitivity of the TCD using H_2 as a carrier gas. It is also necessary to bear in mind that the gas carrier and the substance to be analyzed must be significantly different with respect to molecular weight. For example, for an analysis of oxygen the best results are obtained using Ar ($M = 39.9$) as a carrier gas. For an analysis of N_2 , O_2 , Ne, He, H_2 , /8 CO , CH_4 , NH_3 , H_2O , and several other gases and vapors, good results can be obtained using CO_2 as a carrier gas. For practically all gases and vapors of volatile hydrocarbons up to C_4 , it is possible to use Kr and Xe as carrier gases. Volatile organic compounds with a high molecular weight have been used as carrier gases (such $C_2F_2Cl_2$, $C_2H_4F_2$, and others) [45].

The density detector is also used for detecting aggressive gases (HF, HCl) and others) inasmuch as its sensitive elements are not in contact with the samples to be analyzed [46, 47].

Analysis chromatographs of gas mixtures obtained using a density detector are introduced in Figure 1 [40].

A high linearity is characteristic for the density detector, and calculation is possible, according to the detector readings, of a quantity of a component if its molecular weight is known [38, 39, 48, 49]. Therefore, during work with the density detector, it is not required to make calibrations, other than introducing a 5% correction for carrier gas H_2 , taking into account its high thermal conductivity [39]. When using two or more carrier gases one can measure with an accuracy of 4% tolerance the molecular weight of gases and vapors being analyzed with the goal of identification [50-54].

The VNIKANeftegaz Institute has developed quite simple G-20 and G-21 density detectors for use with universal chromatographs, Models KHT-63 and KHTP-63 [39]. Several foreign firms also produce density detectors, although these detectors have not yet been widely used [42].

4. An Ionization Cross Section Detector (ICD).

/9

Detecting gases and vapors by means of adsorption or radioactive radiation was first suggested in 1953 [55]. The detector had a large working volume and could be used only with the employment of a large flow rate of the carrier gas. The proposed detector had comparatively low sensitivity, but was extremely linear, nearly to the point of a 100% concentration of the sample. The simplicity of design and high linearity were the reasons for the subsequent improvement of the detector; this improvement was also related to a potential possibility of its use for an analysis of planetary atmospheres [56].

Lovelock [57-59] perfected the ionization cross section detector by means of decreasing its working volume, which had been suggested by Martin [60], by using a tritium radioactive source. The detector became approximately 10 times more sensitive to all gases and vapors in comparison with the katharometer. It is necessary to note that the minimal concentrations (C_{min}) which can be observed in the ICD and TCD are equal; however, since the working volume of the TCD (V) is nearly one order of magnitude greater, the minimal detectable quantity ($G_{min} = C_{min} \times V$) is less than that for the TCD. Therefore, the ionization cross section detector can be used with micro-precipitation columns, and is frequently employed in chromatographs which are adapted for space research, upon which severe demands are made with respect to rate and size. A detailed

examination of the physical basis of the ionizational method of detecting the ionization cross section is conducted in the work of Otvos and Stevenson [61], who established that the ionization cross section of molecules for a certain type of radiation is a combination of the component molecules of the cross sections of ionization of atoms and practically does not depend on the nature of the chemical compound being analyzed. A more detailed familiarization with the mechanism of detecting the cross section of ionization may be acquired in a number of published works [58, 59, 62]. The type of ICD presently being used is presented in Figure 2. /10

A necessary condition for the work of the ICD at atmospheric pressure is a predominance of the free path length of beta particles over the dimensions of the detector chamber. For carrier gases with small ionization cross section (H_2 and He) the sensitivity of the detector to stable gases is highest. For carrier gases N_2 , Ar, and CO_2 the sensitivity of the ICD to relatively simple substances is now great [59]. He and Ar are used in the capacity of carrier gases, saturated with water vapor [58] or He with 3% methane [63], with the aim of eliminating metastable atoms of Ar^* and He^* . In a number of works it was suggested to use the ionization cross section detector for analyzing the atmosphere of planets (primarily Mars and Venus) and also for an analysis of substances located in the soil of their surfaces [56, 59, 64, 65]. Chromatographic instruments have also been produced for monitoring the atmospheric components and contents of traces of toxic impurities in the spacesuits of cosmonauts and in the cabin of the "Apollo" spacecraft using a 3-chambered micro-detector of ionization cross section for sequential working in 3 different columns [1]. The diagram of the detector is shown in Figure 3b. With the aim of decreasing the size and weight of the detector, the 3 chambers are arranged coaxially, and a decrease in the size of the chamber increases the sensitivity of the detector but decreases its linearity. In connection with this, for detecting various quantities of components to be analyzed, the chambers of the detector have been manufactured in various dimensions. Sensitivity of a detector for $CO_2 \cdot 10^{-8}$ mmole/ml. It has been shown that one can obtain a sensitivity at less than 10 ppm ($10^{-3}\%$ by volume) for practically all compounds. Notwithstanding the /11

increased attention given to the ICD with the goal of utilizing it for an analysis of space objects, it is necessary to note that ICD has undeservedly not been sufficiently utilized in the practice of gas chromatography and has been everywhere replaced by TCD. However, the possibility of calculating the signals of ICD and its high linearity make its use more prospective with respect to qualitative analysis and doing parallel work with highly selective detectors [62-67]. The characteristics of the ICD are introduced in Tables I and 2.

5. Electron Mobility Detector (EMD).

A detector having high sensitivity to stable gases and based on changes in the mobility of free electrons in an inert gas, in the absence of any other gas, was suggested by Lovelock in 1960 [68].

In inert gases, even in weak electrical fields, electrons acquire energy which significantly exceeds the energy of atoms of the inert carrier gas. Since the mass of an electron is much smaller than the masses of the atoms of the carrier gas, the energy of the electrons is not quite lost during elastic collisions between the electrons and atoms of the inert gas. If a molecule of the gas to be analyzed strikes the detector, the electrons are subjected to a non-elastic collision, as a result of which they completely lose their velocity and will regain it only due to movement in the direction of the field. Hence, in the electron mobility detector, upon the striking of the carrier gas by a substance, the electrons temporarily increase their rate of drift in the direction of the field and one obtains a positive signal. The method of detection with respect to mobility, a plane-parallel design of detector is used with a tritium source and an argon carrier gas (Figure 4). Argon ionizes in a certain region of the ionization chamber at the cathode. To the anode, which is located further from the source than the length of free movement of beta particles, are attached short, right-angled surge voltage devices, because the length of an impulse is selected in such a way that in pure argon the fast electrons, as a result of their slight mobility in an electrical field, cannot congregate on the anode and the background current of the detector will be slight.

/12

During the delivery of a pulse, part of the free electrons collect on the anode; the quantity of electrons is proportionate to the concentration of the gas being analyzed. The detector has differing degrees of sensitivity to various gases, and therefore requires calibration [68, 72].

It is necessary that the carrier gas employed be very pure, in connection with which particular requirements are manifested with respect to the cleanliness of the device and for the packing of columns.

The electron mobility detector can be successfully employed during analysis of gases and vapors contained in the atmosphere. Using it, one can measure water vapor with a high degree of sensitivity. Since the linearity of the detector is not great, it is not recommended to be used with concentrations greater than 0.1% by volume in the carrier gas. Good results are given by the detector during analysis of CO and CO₂.

The basic characteristics of this detector are introduced in Tables 1 and 2.

6. Photoionizational Detector (PID)

A photoionizational detector was suggested by Lovelock in 1960 [73]. The working principles of the PID consist in the fact that in a stream of inert gas, a corona gas discharge of direct current is stimulated. In the discharge, excited atoms of argon are formed, and as a result of their scintillation, a flux of photons with a critical energy is received. An ionization chamber is mounted in the path of the photon flux (Figure 5) which has two collector electrodes, into which the carrier gas from the column passes. Photons either indirectly ionize the sample molecules, or ionization occurs as a result of a transfer of the photon energy through the newly formed metastable argon atoms [73-74].

The sensitivity of the detector depends upon the geometrical shape of the electrodes, the shape of the electrical field of the detector, the regime of its work, and the form of the gas discharge [74-76]. At the present time, several variations of PID have been built, which differ in their methods of creating a photon flux which correspondingly differ in sensitivity, stability, and in other characteristics [72-76].

The photoionizational detector is sensitive not only to carbon dioxide, but also to stable gases whose ionization potential exceeds the energy of metastable atoms of Ar* (11.6 eV). This is apparently related to the fact that in a corona discharge excited atoms of argon also form; these atoms radiate during scintillation of the high energy photons.

The characteristic peculiarity of the PID is the fact that one obtains peaks of reverse polarity or electrically negative gases (O_2 , CF_4 , CCl_4 and others), the formation of which can be explained by a capture of electrons which penetrate the collector chamber from the discharge regions, and by molecules which are initially excited by the photons [74].

It is also necessary to note that in the linear operating region of the detector, normally shaped peaks were also obtained; with significant loading of the detector, peaks were observed with cut [illegible word] and even doubling of peaks [74].

The characteristics of this detector are presented in Tables 1 and 2.

7. Argon Detector (Ar-D).

/14

The basis of work of argon detectors is comprised by processes of exciting atoms of argon to a metastable state and the ionization of molecules of the substance being analyzed by metastable atoms (the Penning effect). These detectors are flow-type ionization chambers which contain a radioactive source of radiation, as rule a beta-source (St^{90} , Pm^{147} , H_I^3 and others) [72, 77-81].

The sensitivity and linearity of argon detectors depends on temperature, the pressure in the detector interior, and on the supply voltage [81-82].

Argon detectors require the use of a quite pure carrier gas. Impurities of oxygen and moisture in argon are especially dangerous. Industrially pure argon, containing oxygen at a level of 10^{-3} by volume percent, is entirely suitable for work. However, it is always necessary to have a means of drying argon to a dew point of -70 to $-80^\circ C$.

The argon detector is sensitive to all substances, whose potential of ionization does not exceed the potential of excitation of metastable argon,

that is eV 11.6. In a mass-produced apparatus, one can quite reliably register the substances being analyzed at a content of 10^{-6} volume percent (0.01 ppm).

Argon detectors are usually compared with plasma-ionization analyzers. However, unlike the latter, argon detectors are capable of analyzing not only organic substances, but also many inorganic substances, such as, for example, H_2S , NO_2 , NO , NH_3 , PH_3 , BF_3 [78, 104]. For example, during analysis of NO [83] on a standard argon detector, the minute of detection was 0.01 μl .

A coaxial design argon detector has also been suggested (Figure 3a), which has high sensitivity to inert gases. The mechanism of detection of inert gases in this case is not entirely clear [84-85]. However, an examination of the possible mechanisms of its work enable one to place it either in the category of discharge or argon beta-ionized detectors [78], or in the category of direct electron mobility detectors [68]. The readings of the detector depend on the molecular weight of the carrier gas and decrease in series: $Xe > Kr > Ne > Ar > He$ (86). The coaxial detector is more sensitive at high temperatures (150-250°C), (Figure 6).

In practice, due to the high cost of Xe and Kr , Ar is used in the capacity of a carrier gas; however, for special purposes, for example during the use of this detector for the proposed chromatographic analysis of the atmosphere of Mars (86) the use of Xe and Kr provides definite advantages (see Table 2).

In view of its slight working volume, the coaxial detector can be used with capillary and micro-precipitation columns [85].

The drawback of the coaxial detector during gas analysis is the necessity of work in a maximum ratio of sensitivity to supply voltage, and in connection with this it is necessary to have a voltage supply installation that is accurate by more than ± 0.01 volts.

The characteristics of the coaxial detector are presented in Tables 1 and 2.

NASA

8. The Indirect Method of Detecting Inorganic Substances with an Argon Detector.

Page One Title

The physical basis and theory of this method, which has been termed the method of indirect measurement of electron mobility, have been examined in a number of works [87-89]. This method was first used by Wilson for analyzing inert gases [90-91].

For accomplishing the method of indirect measurement of electron mobility in the argon detector it is necessary to constantly supply argon mixed with the organic substance (blank sample) and to fix the proportion of the ionized flux during passage of the substance being analyzed through the detector.

The linearity of the detector is limited, since with an increase in the concentration of the substance to be analyzed, the detector signal tends toward saturation. Sensitivity is not high. In a majority of cases one can detect gas constants reliably in a concentration of an order of $10^{-4}\%$ by volume.

Use of the method of indirect measurement of electron mobility causes an increase in the requirements for stabilization of the experimental parameters: the temperature of the detector and the column, the supply of the carrier gas and the voltage. The presence of the blank sample increases the background current of the detector by several times and makes it extremely sensitive to fluctuations in the experimental parameters.

Additional instability in the background current can be caused by fluctuation in the content of binary carrier gas. It is more expedient either to use a blank sample which is not attained by the column, since in this case fluctuations in the temperature of the column and in the supply rate of the carrier gas have a minimal effect on the content of the carrier gas, or to supply it between the column and the detector.

The optimal content of the blank sample in the carrier gas is in a region of concentration which ensures saturation of the signal of the argon detector.

NASA

/16

At present, the following substances are used most frequently in the capacity of a blank sample: Ethylene, acetylene (1-100 ppm) [91] and propane (0.2%) [87].

The difficult problem of dispensing the blank sample gas was solved by Lesser [92] by means of mounting, between the column and the detector, an organic preparation (1, 2, 4, 5, -tetrachlorbenzene) whose vapor tension at a constant temperature is constant, and the molecules of which, together with the carrier gas, entered the detector.

9. A Helium Detector (He-D).

The first helium method of detecting gases with a low boiling point was devised by Berry [93], who used a simple argon detector for this purpose with purified helium in the capacity of a carrier gas. Since the excitation potential of metastable He (19.8 e.V.) exceeds the ionization potential for practically all substances (besides Ne), using a helium detector it is possible to conduct a direct detection of gas constants [94-100]. During the work of a helium detector, a significant influence on the effectiveness of formation is caused by non-elastic collision of electrons with atoms of the mixture, including the mixture being analyzed, which decreases the probability of generation of He.

Dependent on the concentration of the mixture in the original carrier gas, the signal of the helium detector can change not only in magnitude, but also in polarity (Figures 7 and 8). In commercial helium the total content of impurities is at the level of 10^{-2} - $10^{-3}\%$ by volume. In a majority of cases this magnitude exceeds the critical concentration value of impurities C_{cr} .

The purification point of helium at which the total content of impurities becomes actually less than C_{cr} , leads to the appearance of a positive signal in the detector. When using pure helium, the detector has a significantly high level of sensitivity and linearity with a slight background current.

Purity of the carrier gas requires, on the one hand, the necessity of using special systems for purifying helium, and on the other hand, ensuring the purity and hermetic sealing of all the gaslines of the chromatograph.

/17=

In the columns one may only use non-volatile sorbants. At the present time, the most acceptable system of purification is a quite simple adsorptional system of purification, which includes a molecular filter at the temperature of liquid nitrogen. This system, however, does not ensure effective purification of helium from hydrogen. Extremely promising is a diffusion system of purification whose working principles are based on selective diffusion of helium through glass or quartz [103]. It was suggested [95] that one use in the capacity of a helium detector a small chamber with a tritium source of increased activity (Figure 9). In this type of detector, at relatively low voltages, excitation of helium occurs only as the result of collisions with beta-particles. The detector becomes practically insensitive to loading of the carrier gas; however, its sensitivity to gas constants decreases approximately to the point of $10^{-4}\%$ by volume. A significant increase in sensitivity of a similar detector with a tritium source was achieved by means of using pure He and high voltage [101-102]. At present, helium detectors with tritium sources are a part of the structural design of mass-produced chromatographs of a number of foreign firms. All of these require individual calibration of all components in a periodic check of the calibrating characteristics. In work with the chamber of a helium detector, it has been suggested that neon be used in the capacity of a carrier gas [105-106]. At a voltage of nearly 1,000 volts high sensitivity has been obtained for H_2 , O_2 , NO_2 , CO , CO_2 , SO_2 , and other gases. The minimal detectable quantity, for example, for nitrogen was 2×10^{-8} ml. The characteristics of a helium detector are presented in Tables 1 and 2.

10. Discharge Detectors (DD).

There is great interest in detectors of independent discharge or discharge detectors [108-111].

Inasmuch as the discharge detector is simple in design (Figure 10), it is not necessary for this detector, to have a special amplifying device, no radioactive sources are required, and as turned out subsequently, the detector is sensitive as well to gas constants; interest in the use of the properties of electrical discharge for detecting gases and vapors has significantly increase [112].

/19

One can become acquainted with the physical basis of the discharge detector in a number of published works [113-114]. Column discharge detectors working on a direct current at atmospheric pressure are more wide-spread in use as a result of their more stable work and simplicity.

For an analysis of gas constants, one can employ a positive column discharge with carrier gases H_2 , He, or Ar with a minimal sensitivity of $10^{-8} - 10^{-9}$ g/sec. The work of a detector using He as a gas carrier has been most fully studied. As with the helium detectors, detectors using column discharge are extremely sensitive to loading by the carrier gas. With purified helium these detectors can analyze gas constants at a level of 10^{-6} % by volume. Using non-purified helium, the detectors work in the capacity of indirect changes of electron mobility with the sensitivity not greater than 10^{-4} % by volume.

The helium discharge detector, similar to that described by Kärmen [111], in view of its simplicity, compactness, and lack of sensitivity to fluctuations in voltage, as well as its capacity to analyze inorganic gases, has been used in the lunar gas chromatograph [3, 115] for an analysis of gases (H_2 , O_2 , N_2 , CO , CO_2 , H_2O , NH_3 , H_2S , HCN , CH_4 , and others).

The characteristics of a discharge detector are presented in Tables 1 and 2.

11. An Ultrasonic Detector (USD).

Since the speed of a sound passing through a gas depends on the components of the gas and is determined by its density, the work of the USD is based on the measurement of the speed of ultrasound in the gas mixtures [116, 117]. The USD, similar to that developed in the Groznyy affiliate of the VNIKANeftegaz [118] or the one produced by the firm of Micro-tech (USA) [119], is used for analysis of practically all compounds. The detector's readings depend very little on pressure and flow rate of the carrier gas, but quite strongly upon temperature. Therefore, it is necessary that the best thermostatic control and differential designs be used in detecting using this device.

The detector can operate using various carrier gases; it is only necessary that the molecular weight of the gases being analyzed and of the carrier gas

be significantly different [120]. The design and a diagram of the detector are introduced in Figure 11. The non-destructive ultrasonic detector has a small working volume, is quite rapid in operation, and is quite simple. in as much as it does not have any filament or radioactive sources. This detector, probably, will become widely used in gas chromatography, including the analysis of the atmospheres of the Earth and planets.

Chromatograms of an analysis of mixtures in helium using the ultrasonic detector are introduced in Figure 12.

12. High Vacuum Detector (HVD).

The ionization detector, suitable for analysis of both organic and inorganic gases and vapors, can be made by ionizing a molecule of the substance to be analyzed with slow electrons in a high vacuum, as this process occurs in an ion source of a mass spectrometer [121] [122].

During the use of these detectors, which are similar to the ion source of the mass spectrometer, a sensitivity value was obtained which was no worse than the sensitivity of the flame-ionizing detector [123].

The stability of work of the vacuum detector depends on the stability of pressure and ionizing voltage. The characteristics of the detector are listed in Tables 1 and 2.

The mass spectrometer can also be employed as a detector for analyzing gas constants, vapors of volatile organic substances and the products of pyrolysis of complex organic molecules at the outlet of the chromatographic column [124-129].

For analyzing samples of soil on planets with the goal of measuring biologically important compounds in it, a gas chromatograph was built in which, in the capacity of a detector, a simple mass spectrometer was installed for identifying the products of pyrolysis [130]. The weight of such a system, for example, for the analysis of organic compounds on the surface of Mars, was, in all, nearly 7 kg, while the expenditure of energy was approximately 10 W.

NASA

The use of a mass spectrometer in combination with a chromatogram for analysis and identification of various organic and inorganic compounds has been explored in a number of published works [131-132].

13. Emission Detectors. Cover Page Title

For an analysis of gases, two types of emission detectors can be used:

a) High Frequency Emission Detector (HED). It was suggested by MacCormack in 1965 [133]. A discharge is excited from a high frequency emitter in a quartz cube, through which He or Ar passes. Free electrons in the discharge achieve an energy which is sufficient in order to cause a disintegration of molecules which strike the detector. The radiation spectrum obtained in this process is registered by a photomultiplier spectrophotometer. The sensitivity of the detector to gas constants in Ar is 10^{-9} g/sec for N_2 , H_2 , O_2 , NO, 10^{-8} g/sec for He and 10^{-7} g/sec for CO_2 [133]. The expenditure of energy for attaining a stable discharge is greater than 20W, since the intensity of radiation on a specific wavelength characteristics for each compound depends on the power of the high frequency emitter.

b) In the flame-photometric detector (FPD) the radiation of matter falling into the air-hydrogen flame is registered using the measuring part of a standard spectrophotometer [134]. Detection is accomplished on certain long waves characteristic for the specific compound, because the intensity of the characteristic wave length is a quantitative value of the emission of its compound. In FPD such compounds as CO , CO_2 , N_2O_4 , SO_2 , N_2F_4 , HF, and CS_2 , which cannot practically be measured using the flame-ionizing detector, can be detected with a great degree of sensitivity [135-137]. Measurement in the air, for example of SO_2 and H_2S , can be accomplished in the FPD within the range of 0.1-1.3 ppm [138].

14. Detectors for Measuring a Dielectric Constant (DDC).

In 1961 a detector was suggested based on the measurement of the dielectric constant of the substances to be analyzed between two electrodes in a chamber with a carrier gas [140]. The detector is sensitive to a majority of gases with correct selection of the carrier gas; the detector has good linearity.

/22

The minimal detectable quantity is 10^{-10} g/sec for O_2 , N_2 , H_2 , CO_2 , CO , CH_4 , NO_2 , N_2O and SO_2 [139] and is comparable to the sensitivity of ionizing detectors. Linearity for all the gases enumerated above, as well as C_2H_2 , C_2H_6 , C_3H_8 , and NH_3 is equal to 100%. A piezoelectric detector based on the measurement of the dielectric constant has been investigated in a number of works [140-141].

15. Other Types of Detectors.

Several detectors have also been suggested which can analyze only certain compounds.

Phillips used an electrolytic cell for selective detection of O_2 (142). The work of the detector is based on reactions occurring between a silver anode and lead cathode in an electrolyte containing ions of OH^- . The minimal detectable quantity of O_2 is 10^{-5} ml. Linearity is up to 1% concentration O_2 .

A piezoelectric sorption detector [143] is sensitive, for example, only to water vapor employed in the capacity of adsorbent of molecular filters.

There are also other detectors whose use is more limited.

NASA

CONCLUSION:

The data presented above indicate that for analysis of gases and several other volatile organic and inorganic substances, up to the present time, quite a large number of detectors have been suggested. However, some of these are insufficiently sensitive and have insufficient properties of linearity, but the simplicity and reliability of others, which have a higher degree of sensitivity, also have slight linearity and are insufficiently stable in operation. In connection with the use of chromatographs for space research, and, specifically, for an analysis of the atmosphere of the Earth and planets, it is necessary to consider as ideal a highly sensitive detector (with a sensitivity not less than $10^{-5}\%$) which detects practically all compounds; this detector has a high linearity (within the range of up to 100% concentration) and whose work practically does not depend upon experimental parameters (temperature, flow rate of gases, pressure, voltage, and other factors). Such a detector has not been created up to the present time. Therefore, the goal of the given work is, on the basis of the example of an examination of currently-used detectors, to direct the attention of a wider circle of specialists and workers in various fields of science and technology toward a solution of this problem.

NASA

Table 1: The Characteristics of Basic Types of Detectors for Analyzing Gases.
Page One Title

Detector	Carrier Gas	Potential V	Back ground	Noise	Linearity	Sensitivity	Non electrical	
			Current A	level A			Expenditure of energy in volts	Weight in kg
1	2	3	4	5	6	7	8	9
Kathometer	H ₂ ; He ; N ₂ Ar.	9 - 12	Bridge current 0,2	5-20 μV	10 ⁴ (He)	10 ⁻⁶ mg/ml	~ 2	0,5-1
Thermistor	- " -	3 - 6	- " - 0,01	5-10 μV	10 ³ (He)	3.10 ⁻⁶ mg/ml	~ 0,5	0,5
ρ density analyzer	Ar ; N ₂ ; CO ₂ ; air	9 - 12	- " - 0,2	5-20 μV	10 ⁴ (N ₂)	5.10 ⁻⁵ mg/ml	~ 2	1-2
Ionization cross-section analyzer	H ₂ ; Ar ; H ₂ + 3% CH ₄	1 - 5; 300-1000	10 ⁻⁸ - 10 ⁻⁹	10 ⁻¹³	5.10 ⁵	10 ⁻¹¹ g/sec CH ₄	< 0,2	0,2

1	2	3	4	5	6	7	8	9
direct electron mobility detector	Pure Ar	50-100 pulses	3.10 ⁻⁹	10 ⁻¹³	3.10 ³	10 ⁻¹¹ F.CO ₂	< 0,1	0,2
Photoionization detector	Ar ; He ; N ₂	100-200; discharge 2 kv	10 ⁻¹⁰	10 ⁻¹²	10 ⁴	1,5.10 ⁻¹¹ g/sec O ₂ ; N ₂	~ 2	0,5-1
Argon detector	Ar.	750-2000	10 ⁻⁹ - 10 ⁻¹⁰	10 ⁻¹¹ - 10 ⁻¹⁴	10 ⁴ - 10 ⁶	10 ⁻⁷ - 10 ⁻⁹ mg/ml 0,01 mm Hg NO	0,5	0,2
Coaxial argon detector	Ar.	1-4 gases; 100-250.	3.10 ⁻⁹	1.10 ⁻¹²	~ 500	5.10 ⁻¹² mole/sec CO ₂ ; CH ₄	< 0,1	0,2
Indirect electron mobility detectors	Ar + blank sample He tech.	750-1250	3.10 ⁻⁸	10 ⁻¹¹	~ 300	2-6.10 ⁻⁸ ml H ₂ O ₂ ; N ₂ ; CO	< 0,1	0,2

NASA

Continuation of Table 1.
Page One Title

Reproduced from
best available copy.



I	2	3	4	5	6	7	8	9
Helium	He Non-pure	100-300	10^{-11}	10^{-13}	10^3	0,003 ppm, CO; O ₂ ; CH ₄	< 0,1	0,2
Discharge	H ₂ ; He; Ar	500-2000	< 5-10 μ A	< 0,01 A	10^4	$5 \cdot 10^{-7}$ mg/ml	1,0	0,1
Ultrasonic	any gas	10 MHz	-	-	10^6	0,002% H-butane	2,0	1,0
High vacuum	He non-pure; $5 \cdot 10^{-7}$ mm Hg	20-30	$1-2 \cdot 10^{-9}$	$2-3 \cdot 10^{-11}$	10^4	10^{-6} % N-pentane	< 0,1	0,2

Table-2: Threshold Sensitivity of Several Types of Detectors.

Detectors	Gases							Literature references
	H ₂	O ₂	CO ₂	CO	CH ₄	N ₂	Ar	
I	2	3	4	5	6	7	8	9
Kathometer; thermistor; density detector.	$10^{-6}-10^{-8}$ mole	10^{-8} mole	20ppm	$10^{-6}-10^{-8}$ mole	- " -	- " -	- " -	9, 11
Ionization cross-section detector g/sec	$1 \cdot 10^{-11}$	$3-5 \cdot 10^{-10}$	$3-5 \cdot 10^{-10}$	$2 \cdot 10^{-11}$ mole/ml	$1 \cdot 10^{-11}$	$3-5 \cdot 10^{-10}$	-	58, 59
Helium; ppm.	0,02	0,003	0,0008	0,003	0,0035	0,015	-	101

Continuation of Table 2.
Page One Title

Reproduced from
best available copy.



1	2	3	4	5	6	7	8	9
Coaxial argon detector ; mole/sec	$2.4 \cdot 10^{-11}$	$1.2 \cdot 10^{-11}$	$7.6 \cdot 10^{-12}$	$1.8 \cdot 10^{-11}$	$5.5 \cdot 10^{-12}$	$5.5 \cdot 10^{-11}$	-	86
	$1.3 \cdot 10^{-11}$	$0.5 \cdot 10^{-11}$	$4.0 \cdot 10^{-12}$	$0.8 \cdot 10^{-11}$	$2.5 \cdot 10^{-12}$	$2.8 \cdot 10^{-11}$	-	86
	$0.9 \cdot 10^{-12}$	$9.8 \cdot 10^{-12}$	$2.6 \cdot 10^{-12}$	$0.5 \cdot 10^{-11}$	$1.8 \cdot 10^{-12}$	$1.5 \cdot 10^{-11}$	$3 \cdot 10^{-8}$	86
Discharge; g/sec.	$2 \cdot 10^{-9}$	$6.4 \cdot 10^{-8}$	-	-	$1.3 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$	-	112
Indirect electron mobility; g/sec	$3.8 \cdot 10^{-10}$	$3.0 \cdot 10^{-9}$	$4.2 \cdot 10^{-10}$	$2.6 \cdot 10^{-9}$	$8.0 \cdot 10^{-10}$	$3.9 \cdot 10^{-9}$	-	87
Direct electron mobility; ppm	1,0	2,0	$0,6 \cdot 10^{-11} \text{ r.}$	0,6	1,0	0,2	-	69
Ultrasonic, ppm.	0,01-0,5	-	-	-	-	-	-	119

1	2	3	4	5	6	7	8	9
Flame-photometric, [ppm.]	-	-	<100	-	<25	-	-	136
High frequency emission; g/sec	$2 \cdot 10^{-9}$	$4 \cdot 10^{-9}$	$1 \cdot 10^{-7}$	-	-	$9 \cdot 10^{-10}$	-	133
High vacuum, mole/sec.	$6,7 \cdot 10^{-11}$	$1,2 \cdot 10^{-11}$	$0,8 \cdot 10^{-11}$	$1,5 \cdot 10^{-11}$	$1,4 \cdot 10^{-11}$	$1,6 \cdot 10^{-11}$	$0,6 \cdot 10^{-11}$	122.

NASA

REFERENCES

1. Huebner, V.H., Eaton, H.G., Chaudet, J.H., *J. of Gas Chromatog.*, Vol. 4, pp. 121, 1966.
2. Wilhite, W. F., *J. of Gas Chromatog.*, Vol. 4, pp. 47, 1966.
3. Wilhite, W. F., Burnell, M. R., *J.S.A. - Journal*, pp. 53, 1963.
4. Wilhite, W. F., Hollis, O. L., *J. of Gas Chromatog.*, Vol. 6, pp. 84, 1968.
5. Altshuller, A.P. in the book "Advances in Chromatography" edited by J. C. Giddings and R. A. Keller, New York, Vol. 5, pp. 229, 1968.
6. Juvet, R. S., Zado, F. M. in the book "Advances in Chromatography" edited by J. S. Giddings and R. A. Keller, New York, Vol. 2, pp. 249, 1965.
7. Dal Nogare S., Juvet, R. S., *Anal. Chem.*, Vol. 38, pp. 61, 1966.
8. Nogare, S., Dzhuvet, R. S., "Gazo-Zhidkostnaya Khromatografiya (Gas Liquid Chromatography)," published by "Nedra", Leningrad, pp. 209, 1966.
9. Brazhnikov, V. V., Sokadynskiy, K. I., "Gazavaya Khromatografiya (Gas Chromatography)," published by NIITEKHIM, No. 10, pp. 200, Moscow, 1969.
10. Keylamans, A., "Khromatografiya Gazov (Gas Chromatography)," published by "IL," Moscow, 1959.
11. Shinglyar, M., "Gazavaya Kromatografiya v Praktike (Gas Chromatography in Practice)," published by "Khimiya", Moscow, 1964.
12. Gol'bert, K. A., Vigdergauz, M. S., "Kurs Gazavay Khromatografii (The Course of Gas Chromatography)," published by "Khimiya," Moscow, 1967.
13. Winefordner, J.D., Glenn, T. H. in the book "Advances in Chromatography," edited by J. G. Giddings and R. A. Keller, Vol. 5, pp. 263, 1968.
14. Lawson, A. E., Miller, J. M., *J. of Gas Chromatog.*, Vol. 4, pp. 273, 1966.
15. Johnson, R. E., "Progress in Industrial Gas Chromatography," *Plenum Press*, Vol. 1, pp. 163, 1961.
16. Littlewood, A. B., "Gas Chromatography," *Acad. Press*, New York, pp. 302-347, 1962.
17. Purcell, J. E., Ettre, L. S., *J. of Gas Chromatog.*, Vol. 3, pp. 69, 1965.
18. Panson, A. G., Adams, L.M., *Ibid.*, Vol. 2, pp. 164, 1964.
19. Baum, E. H., *Anal. Chem.*, Vol. 36, pp. 438, 1964.
20. Villermoux, M. J., *Bull. Soc. Chim. France*, pp. 699, 1962.
21. Bocheman, J., Purnell, J. H., *J. Appl. Chem.*, Vol. 8, pp. 433, 1958.
22. Brazhnikov, V. V., Volkov, S. A., Sokadynskiy, K. I., "Gazavaya Khromatografiya (Gas Chromatography)," published by NIITEKHIM, No. 1., pp. 84, 1964.
23. Miller, J. M., Lawson, A. E., *Anal. Chem.*, Vol. 37, pp. 1572, 1965.
24. Jordan, J., Kebbekus, B. B., *Anal. Chem.*, Vol. 37, pp. 1348, 1965.
25. Locke, D. C., Brandt, W. W., "Gas Chromatography - 1963", *Acad. Press*, New York, pp. 55-76, 1963.
26. Hoffmann, R. L., Evans, C. D., *J. of Gas Chromatog.*, Vol. 4, pp. 198, 1966.
27. Hara Nobuyoshio, Yamano Susumu, *Kogyo Kagaku Zasshi*, Vol. 66, pp. 1801, 1963.
28. Ray, N. H., *Nature*, Vol. 182, pp. 1663, 1958.

29. Madison, J. J., *Anal. Chem.*, Vol. 30, pp. 1859, 1958.
30. Miller, J. M., Lawson, A. E., *Ibid*, Vol. 37, pp. 1348, 1965.
31. Simmons, M. C., Taylor, L. F., *McGraw-Hill*, *Ibid*, Vol. 32, pp. 731, 1960.
32. Sakodyskiy, K. I., "Gazovaya Khromatografiya (Gas Chromatography)," published by NIITEKHIM, Issue 2, pp. 5, Moscow, 1964.
33. Cowan, C. B., Stirling, P. C., *Verin's Book "Gas Chromatography,"* edited by V. J. Coates, H. J. Noebels, I. S. Fagerson, Acad. Press, New York, pp. 165, 1958.
34. Chizhkov, B. P., Skorniyakov, E. P., 2-aya Vsesoyuznaya Konferentsiya, po gazovoy khromatografii (The Second All-Union Conference on Gas Chromatography), pp. 68, March, 1962.
35. Martin, A. J. P., U.S. Patent 2,728,219, December 27, 1955.
36. Johnson, B. A., *J. of Chromatog.*, Vol. 4, pp. 429, 1960.
37. Martin, R. L., *Anal. Chem.*, Vol. 32, pp. 336, 1960.
38. Nerheim, A. G., *Ibid*, Vol. 35, pp. 1640, 1963.
39. Datskeyich, A. A., "Gazavaya Khromatografiya (Gas Chromatography)," published by NIITEKHIM, Issue 1, pp. 79, Moscow, 1964.
40. Anon., "Gow-Mac Gas Density Detectors," Bulletin Gade 2-64-2M, Bulletin Gade 1-5, 1966. Cover Page Source
41. Guillemin, C. L., Auricourt, M. F., *JasGas Chromatog.*, Vol. 1, No. 10, pp. 24, 1963.
42. Anon., "Technical Newsletter," Gow-Mac Instrument Co., USA, 1968.
43. Guillemin, C. L., Auricourt, M. F., *J. Gas Chromatog.*, Vol. 2, No. 5, pp. 156, 1964.
44. Martin, A. J. P., James, A. T., *Biochem. J.*, (Vol. 63 (1)), pp. 138, 1956.
45. Parsons, J. S., *Anal. Chem.*, Vol. 36, pp. 1849, 1964.
46. Ellis, J. E., Forrest, C. W., Allen, P. L., *Anal. Chim. Acta.*, Vol. 22, pp. 27, 1960.
47. Brazhnikov, V. V., Gur'yev, N. A., Sakodyskiy, K. I., "Gazovaya Khromatografiya (Gas Chromatography)," Issue 1, pp. 27, Moscow, 1967.
48. Martin, R. L., Winter, J. C., *Anal. Chem.*, Vol. 31, pp. 1954, 1959.
49. Munday, C. W., Primavesi, G. R., in the book "V. P. Chromatography," edited by D. H. Desty, Acad. Press, New York, pp. 146, 1957.
50. Nerheim, A. G., U. S. Patent 3,082,618, March 26, 1963.
51. Parson, T. G., *Z. Physic. Chem.*, Vol. 156, pp. 86, 1961.
52. Borisov, F. N., Voronkov, M. G., Dolgov, B. N., *Doklady AN SSSR*, No. 114, pp. 93, 1957.
53. Phillips, G. S. G., *J. Chromatog.*, Vol. 5, pp. 131, 1961.
54. Liberti, A., Conti, A., Crescenzi, V., *Nature*, Vol. 178, pp. 1067, 1956.
55. Pompeo, D. J., Otvos, J. W., (Schell Develop. Co.), U.S. Patent, 1953.
56. Wilson, E. M., Vango, S., Oyama, V., "Gas Chromatography," edited by N. Brenner, Acad. Press, New York, 1962.
57. Lovelock, J. E., *J. Chromatog.*, Vol. 1, pp. 25, 1958.
58. Lovelock, J. E., Shoemaker, G. R., Zlatkis, A., *Anal. Chem.*, Vol. 35, pp. 450, 1963.
59. Simmonds, P. G., Lovelock, J. E., *Anal. Chem.*, Vol. 35, pp. 1345, 1963.
60. Martin, A. J. P., "Vapour Phase Chromatography," edited by D. H. Desty, Butterworths, London, 1957.
61. Otvos, J. W., Stevenson, D. P., *NASA Am. Chem. Soc.*, Vol. 35, pp. 1754, 1963.

62. Abel, K., Schmertaing, H., *Anal. Chem.*, Vol. 35, pp. 1754, 1963.
63. Dimick, K. P., Rigali, L. A., *Aerograph Technical Bulletin*, W113, 1/24/64.
64. Oyama, V. I., Vango, S. P., Wilson, E. M., *ARS Journal*, pp. 354, March 1962.
- 5 65. Schmidt, D., "Proceedings of the Symposium on Lunar and Interplanetary Space Studies," Munich, April 22, 1966.
66. Brazhnikov, V. V., Sakodinsky, K. I., "Gazovaya Khromatografiya (Gas Chromatography)," NIITEKHIM, Issue VI, pp. 11, Moscow, 1967.
67. Brazhnikov, V. V., Gur'ev, M. V., Sakodinsky, K. I., "Chromatog. Reviews," edited by M. Lederer, Vol. 12, pp. 2, Elsevier, Amsterdam, 1970.
- 10 68. Lovelock, J. E., *Nature*, Vol. 187, pp. 49, 1960.
69. Smith, V. N., Fidiom, J. F., *Anal. Chem.*, Vol. 36, pp. 1739, 1964.
70. Mironov, A. S., Petukhova, Ye. P., 3rd All-Union Conference on Gas Chromatography, Abstracts (in Russian), pp. 53, Moscow, May 1964.
- 15 71. Mironov, A. S., Vinogradova, R. G., Dobkin, I. P., Yanovsky, M. I., Gaziev, G. A., "Gazovaya Khromatografiya (Gas Chromatography)," pp. 402 (in Russian), Dzerzhinsk, 1966.
72. Lovelock, J. E., *Anal. Chem.*, Vol. 33, No. 2, pp. 162, 1961.
73. Lovelock, J. E., *Nature*, Vol. 188, pp. 401, 1960.
- 20 74. Kazakevich, V. Ye., "Gazovaya Khromatografiya (Gas Chromatography)," NIITEKHIM, Issue II, pp. 47, Moscow, 1964.
75. Mikiya Yamane, *J. Chromatog.*, Vol. 9, pp. 162, 1962; Vol. 11, pp. 172, 1963; Vol. 14, pp. 355, 1964.
76. Mironov, A. S., Vinogradova, R. G., 3rd All-Union Conference on Gas Chromatography, Abstracts (in Russian), pp. 52, Moscow, May 1964.
- 25 77. Frank, Ya. A., Yanovski, M. I., "Kinetika i Kataliz," Vol. 2, pp. 292, 1961.
78. Lovelock, J., "Gas Chromatography," "Mir", pp. 28, Moscow, 1964.
79. Condon, R., Shelly, P., Averill, V., *Ibid*, pp. 45.
- 30 80. Matoushek, S., *Ibid*, pp. 90.
81. Knapp, J. Z., Meyer, A. S., *Anal. Chem.*, Vol. 36, pp. 1430, 1964.
82. Rotin, V. A., "Zavodskaya laboratoriya," No. 11, pp. 1446, 1967.
83. Kipping, P. F., Jeffery, P. G., *Nature*, Vol. 200, No. 4913, pp. 1314, 1963.
84. Lipsky, S. R., Shahin, M. M., *Nature*, Vol. 197, pp. 625, 1963.
- 35 85. Shahin, M. M., Lipsky, S. R., *Anal. Chem.*, Vol. 35, pp. 467, 1963.
86. Lipsky, S. R., Shahin, M. M., *Nature*, Vol. 200, pp. 566, 1963.
87. Bothe, H. K., Leonhardt, *J. Chromatog.*, Vol. 19, pp. 1, (1965).
88. Laudowne, R. A., Lipsky, S. R., *Nature*, Vol. 189, pp. 571, 1961.
89. Krug, H., Werner, E., 5th Symposium on Gas Chromatography, pp. 293, Berlin, May 1965.
- 40 90. Willis, V., *Nature*, Vol. 184, pp. 894, 1959.
91. Willis, V., U. S. Patent 3,117,225, Jan. 7, 1964.
92. Lesser, R., *Angew. Chem.*, Vol. 72, pp. 631, 1960; Vol. 72, pp. 775, 1960.
93. Berry, R., *Nature*, Vol. 188, pp. 578, 1960.
- 45 94. Berry, R., "Gas Chromatography," edited by M. Van Swaay, pp. 321, Butterworths, London, 1962.
95. Rotin, V. A., 3rd All-Union Conference on Gas Chromatography, Abstracts (in Russian), pp. 49, Moscow, May 1964.
96. Rotin, V. A., "Gazovaya Khromatografiya," NIITEKHIM, Issue IV, pp. 53, Moscow, 1966.
- 50 97. Wiseman, W. A., *Nature*, Vol. 190, pp. 1187, 1961; Vol. 192, pp. 964, 1961.

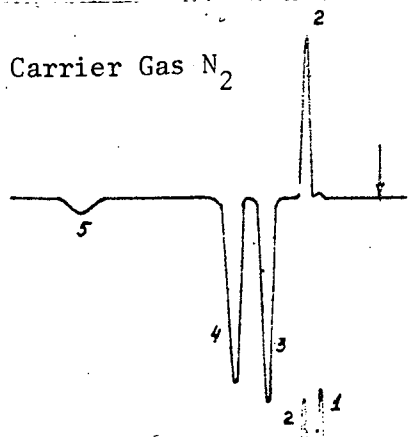
98. Ellis, J. F., Forrest, C. W., *Anal. Chim. Acta.*, Vol. 24, pp. 329, 1961.
99. Karmen, A., Guiffrida, L., Bowman, R. L., *J. Chromatog.*, Vol. 9, pp. 13, 1962.
Page One Title
- 5 100. Bourke, P. J., Dawson, R. W., Denton, W. H., *J. Chromatog.*, Vol. 14, pp. 387, 1964.
101. Hartmann, C. H., Dimick, K. P., *J. Gas Chromatog.*, Vol. 4, pp. 163, 1966.
102. Hartmann, C. H., Dimick, K. P., *Varian Aerograph/Technical Bulletin*, 118-65.
- 10 103. Anon., Electron Technology, Inc., New York, *J. Gas Chromatog.*, Vol. 6, No. 11, pp. 15A, 1968.
104. Sakaida, R. R., Rinker, R. G., Guffel, R. F., Corcoran, W. H., *Anal. Chem.*, Vol. 33, pp. 32, 1961.
105. Gnouck, G., *Z. Analyt. Chem.*, Vol. 189, pp. 124, 1962.
- 15 106. Gnouck, G., "Gazovaya Khromatografiya v 1961," Gostoptechizdat, pp. 64, 1963.
107. Chier, S. J., Bauer, A. S., *Silikat Tech.*, Vol. 14, pp. 119, 1963.
108. Harley, J., Pretorius, V., *Nature*, Vol. 178, pp. 1214, 1956.
109. Karmen, A., Bowman, R. L., "Gazovaya Khromatografiya," Foreign Languages Publishers, pp. 398, 1960.
over Page source
- 20 110. Evard, E., Thavelin, M., Joosens, J. V., *Nature*, Vol. 193, pp. 59, 1962.
111. Karmen, A., Bowman, R. L., *Nature*, Vol. 196, pp. 62, 1962.
112. Markevich, A. V., Dobychin, S. G., Mel'nik, A. P., "Gazovaya Khromatografiya," NIITEKHIM, Issue I, pp. 43, Moscow, 1964; Issue II, pp. 42.
- 25 113. Okhotnikov, B. P., Datskevich, A. A., "Gazovaya Khromatografiya," Dzerzhinsk, pp. 377 (in Russian), 1966. (4')
114. Markevich, A. V., Dobychin, S. L., *Ibid*, pp. 382.
115. Weber, T. B., "Lectures in Aerospace Medicine," pp. 327-346, Washington, D. C., 1962.
- 30 116. Bergman, A., "Ultrazvuk," Publ. House "Nauka," 1956.
117. Martin, A. E., *Nature*, Vol. 178, pp. 407, 1956.
118. Volkov, Ya. F., "Gazovaya Khromatografiya," Dzerzhinsk, pp. 363, 1966.
119. Anon., "Micro-tek Ultrasonic Detector, Model U-70," *Bulletin-Micro-Tek Unicam*, 1968.
- 35 120. Noble, F. W., Abel, K., Cook, P. W., *Anal. Chem.*, Vol. 36, pp. 1421, 1964.
121. Ryce, S. A., Bryce, W. A., *Nature*, Vol. 179, pp. 541, 1957; *Can. J. Chem.*, Vol. 35, pp. 1293, 1957.
122. Krylov, B. K., "Gazovaya Khromatografiya," NIITEKHIM, Issue IV, pp. 48, Moscow, 1966.
- 40 123. Brunce, C., Jenckel, L., *Z. Anal. Chem.*, Vol. 197, pp. 42, 1963.
124. Donner, W. T. J., Gallaway, W. S., *Anal. Chem.*, Vol. 29, pp. 1378, 1957.
125. Gohlke, R. S., *Ibid*, Vol. 29, pp. 1793, 1957.
126. Holmes, J. C., Morrell, F. A., *Appl. Spectroscopy*, Vol. 11, pp. 86, 1957.
127. Orlov, V. Yu., Gur'ev, M. V., "Gazovaya Khromatografiya," NIITEKHIM, Issue V, pp. 57, Moscow, 1967.
- 45 128. Talroze, V. L., "Pribory i Tekhnika Eksperimenta," Vol. 10, No. 6, pp. 130, 1965.
129. Talroze, V. L., Skurat, V. Ye., Karpov, G. V., Zh. F. Kh., XLIII, Issue 2, pp. 452 (in Russian), 1969.
- 50 130. Bentley, K. E., Whitten, D. G., ^{NASA}Giffin, C. E., Wilhite, W. F., "Towards Space Penetration," *Am. Astron. Soc.*, pp. 93, New York, 1964.

131. Bentley, K. E., Giffin, C. E., Whitten, D. G., Wilhite, W. F., *Analys. Instr.*, Plenum Press, pp. 113-125, New York, 1965.
132. Simmons, P. G., Shulman, G. P., O'Stembridge, C. J., *J. of Chromatog. Science*, Vol. 7, No. 1, pp. 36, 1969.
- 5 133. McCormak, A. J., Tong, S. C., Cooke, W. D., *Anal. Chem.*, Vol. 37, pp. 1470, 1965. Cover Page Title
134. Juvet, R. S., Durbin, R. P., *Anal. Chem.*, Vol. 38, pp. 565, 1966.
135. Zado, F. M., Jevet, R. S., *Ibid*, Vol. 38, pp. 569, 1966.
- 10 136. Braman, R. S., *Anal. Chem.*, Vol. 38, pp. 734, 1966.
137. Anon., "Flame-Photometric System," Micro-Tek Instruments Corp., Bulletin AB-110, 1968.
138. Grider, W. L., *Anal. Chem.*, Vol. 37, pp. 1720, 1965.
139. Winefordner, J. D., Williams, H. P., Miller, C. D., *Anal. Chem.*, Vol. 37, pp. 161, 1965.
- 15 140. Winefordner, J. G., Steinbrecher, D., Lear, W. E., *Ibid*, Vol. 33, pp. 515, 1961.
141. Johansson, G., *Ibid*, Vol. 34, pp. 914, 1962.
142. Hillman, G. E., Lightwood, J., *Ibid*, Vol. 38, pp. 1430, 1966.
- 20 143. King, W. N., *Ibid*, Vol. 36, pp. 1735, 1964. Cover Page Source

(4'')

NASA

a. Carrier Gas N_2



b. Carrier Gas CO_2

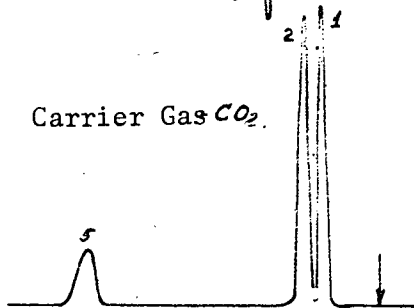


Figure 1.

Figure 1. Chromatograms Obtained on a Density Detector Using Nitrogen as a Carrier Gas (a), and Carbon Dioxide gas; (b). Flow rate of the gas carrier 60 ml/min; comparative flow rate - 80 ml/min; bridge current - 17 bma.

1. N_2 (molecular weight - 28);

2. CH_4 ($M = 16$); 3. CO_2 ($M = 44$);

4. N_2O ($M = 44$); 5. C_2H_6 ($M = 30$).

Page Source

(411)

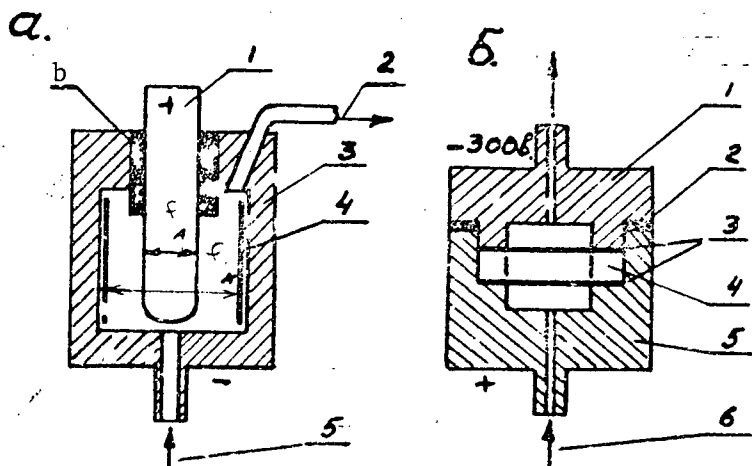


Figure 2.

Figure 2. The Structure of Detectors for Measuring Ionization Cross Section (a) coaxial detector with Cs^{90} radioactive source.

1. Anode; 2. Gas outlet; 3. Detector chamber and the cathode; 4. Radioactive source; 5. Gas inlet to the detector from the column; 6. Insulator.

b. Microdetector with H^3 radioactive source.

1. Cathode; 2. Insulator; 3. Linear radioactive sources; 4. Insulator; 5. Anode; 6. Gas inlet into the detector from the column.

NASA

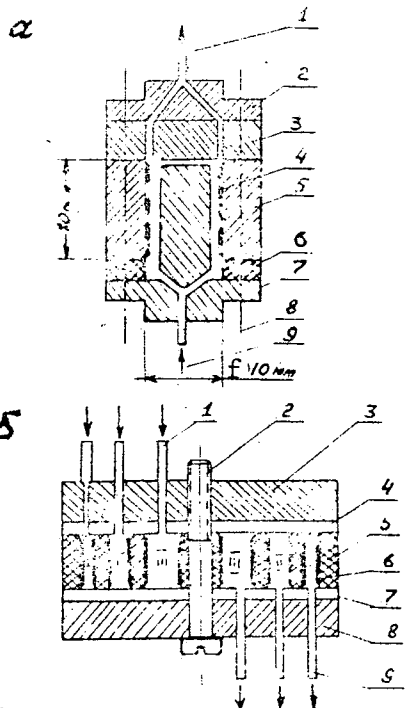


Figure 3.

Figure 3. Line Diagram of Coaxial Detectors:

(a) Single chamber argon detector:

1. Outlet of gas from the detector;
2. Top; 3. Insulator; 4. Tritium radioactive source (200 microcuries);
5. Cathode and detector chamber;
6. Insulator; 7. Anode; 8. Volts;
9. Outlet of gas into the detector from the column.

(b) Three chamber coaxial detector for measuring ionization cross section.

1. Outlet of gases into the detector from the column; 2. Volts; 3. and 8.
- Top, 4. cathode; 5. ring made of polyfluorethylene resins; 6. Tritium radioactive sources (6 pieces); 7. anode;
9. Gas outlets from the detector; I, II, III - Detector chambers.

(411)

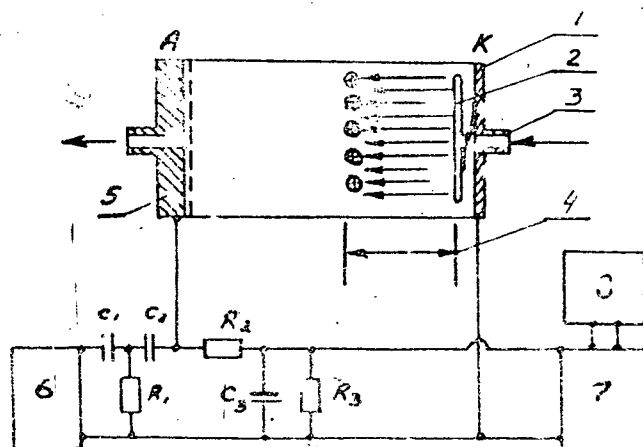


Figure 4.

Figure 4. Design of a Detector of Electron Mobility.

1. Detector housing and cathode (K)
2. Radioactive source (H^3)
3. Inlet for the carrier gas (Ar) through the detector from the column
4. Ionization zone
5. Latticed anode (A) and gas outlet from the detector
6. Square pulse generator
7. Electrometric amplifier
8. Potentiometer

$C_1 = C_2 = 10^{-9}$ farads; $C_3 = 10^{-10}$ farads; $R_1 = 10^5$ ohms; $R_2 = 10^8$ ohms; $R_3 = 10^9$ ohms.

NASA

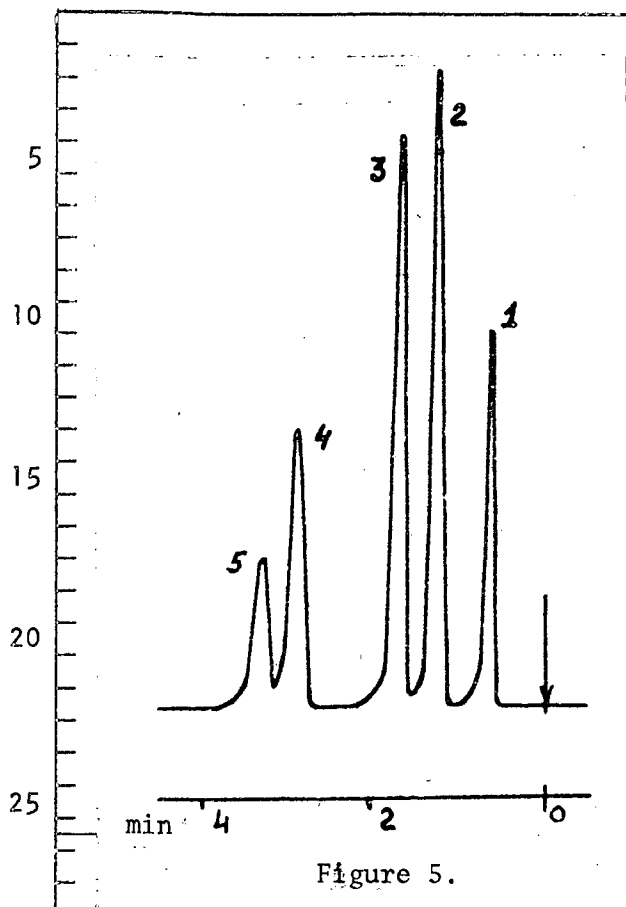


Figure 5. A diagram of a Photoionization
e One Detector.

1. Ionizer needle and inlet of the
r Page supplementary gas stream;
2. Diaphragm; 3. Collector electrodes;
4. Gas outlet; 5. Polarizing electrode
and inlet of the carrier gas from the
column; 6. Region of discharge.

r Page Source

(4'')

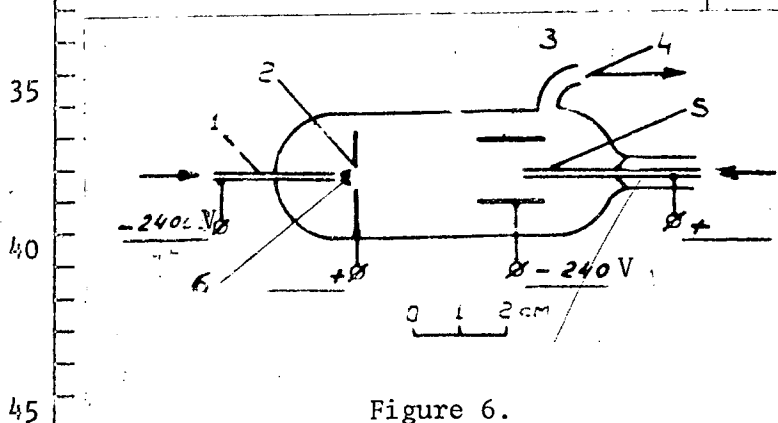


Figure 6. Chromatogram Analysis
of Gas Constants in a Coaxial
Detector.

Temperature of the Detector -
165°C; Voltage - 1.34 volts;
Carrier gas - Ar; Radioactive
source - 200 microcuries; Back-
ground current - 6.1×10^{-9} A;
Noise level - 1.8×10^{-12} A; column
length - 2.4 m, diameter 3 mm with
molecule sieves 5A; column
temperature - 110°C.

1. He - 2 μ l; 2. O₂ - 1 μ l;
3. N₂ - 1 μ l; 4. CH₄ - 0.07 μ l;
5. CO - traces.

NASA

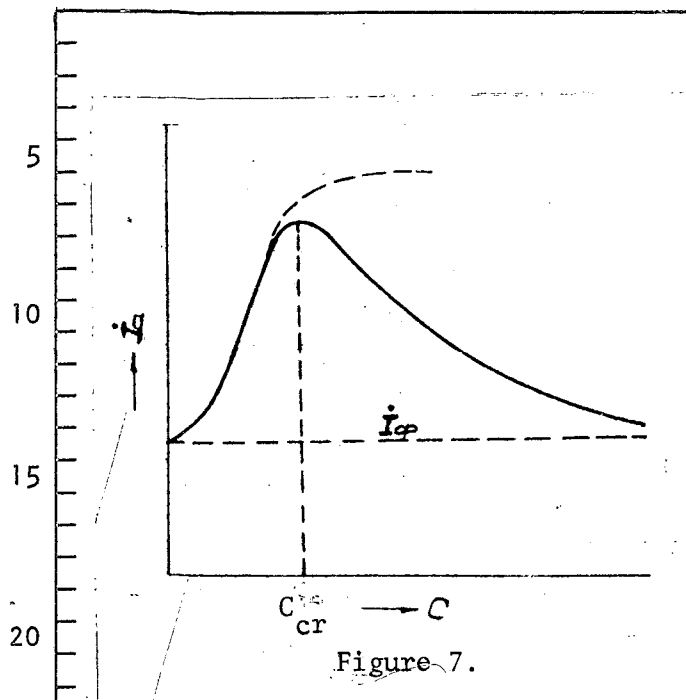


Figure 7. Dependence of Flow of a Helium Detector on the Concentration of Impurities in Helium.

Figure Title

i_f - Background flow

C_{cr} - Critical concentration

Figure Source

(411)

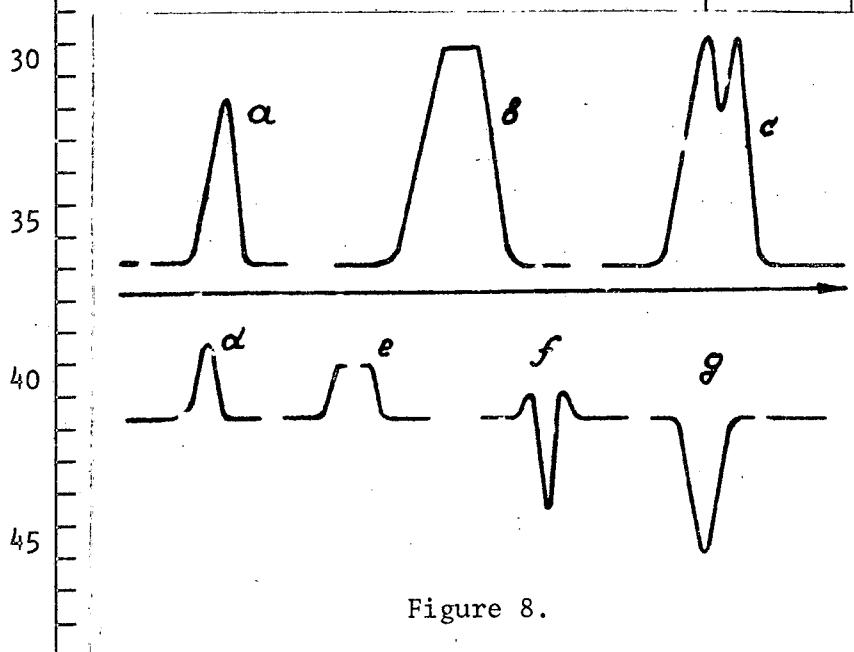


Figure 8. Forms of Peaks of a Helium Detector.

a, b, c - pure carrier gas, concentration of the substance being analyzed increases from a to b; d, a, f, g - concentration of the substance being analyzed is constant, the quantity of impurities in the carrier gas increases from d to g.

NASA

5
10
15
20
25
30
35
40
45
50

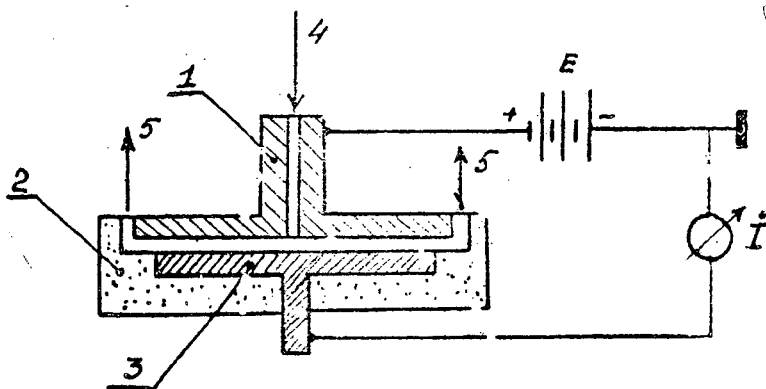


Figure 9.

Figure 9. Schematic of a Helium Detector with a Tritium Source.

- 1. Anode; 2. Insulator;
- 3. Tritium source (cathode);
- 4. Inlet of carrier gas;
- 5. Outlet of gas.

E - Constant voltage source
I - Ionization of flux measuring device.

Cover Page Source

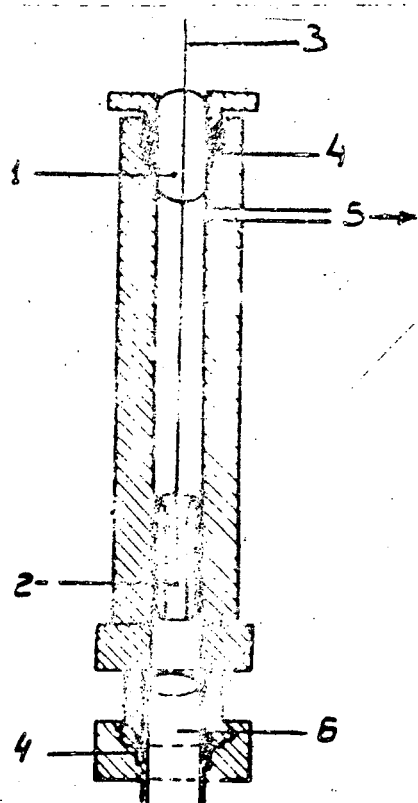


Figure 10.

Figure 10. Structure of a Discharge Detector.

- 1. Insulator (4.11)
- 2. Discharge integral
- 3. Electrode
- 4. Packing
- 5. Gas outlet
- 6. Chromatographic column

NASA

5
10
15
20
25
30
35
40
45
50

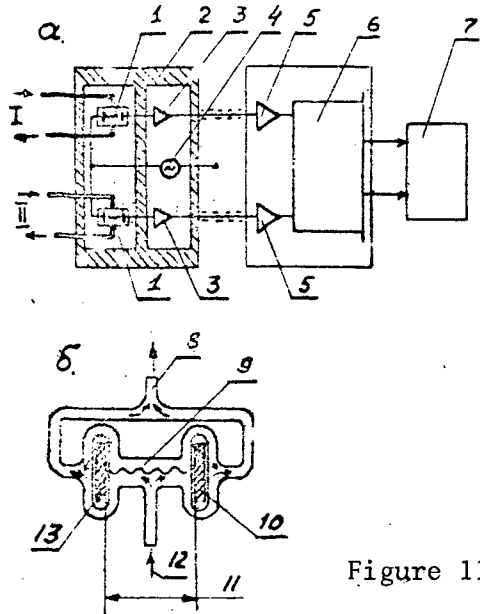


Figure 11.

Figure 11. Ultrasonic Detector (119).

One Title
(a) Electric schematic of the detector;
(b) Design of the detector cell.

Page Title
1. Comparative (1) and working (p) detector cells; 2. Thermostat; 3. Preamplifier; 4. Ultrasonic generator; 5. Amplifier; 6. Electronic schematic; 7. Potentiometer; 8. Gas outlet; 9. Soundwaves; 10. Receiver; 11. Chamber base; 12. Gas outlet from column; 13. Transmitter.

Page Source

(411)

Figure 12. Chromatogram Analysis of Gas Traces in the Helium in the Ultrasonic Detector.

Column length - 3 m, diameter 3 mm; Filler - molecular filter 5A; temperature of column - 150°C; carrier gas - Helium; flow rate - 19 ml/min; sample - 0.76 ml.

1. H_2 - 100 ppm; 2. $Ar + O_2$ - 5 ppm; 3. N_2 - 9 ppm;
4. Kr - 10 ppm; 5. Xe - 26 ppm.

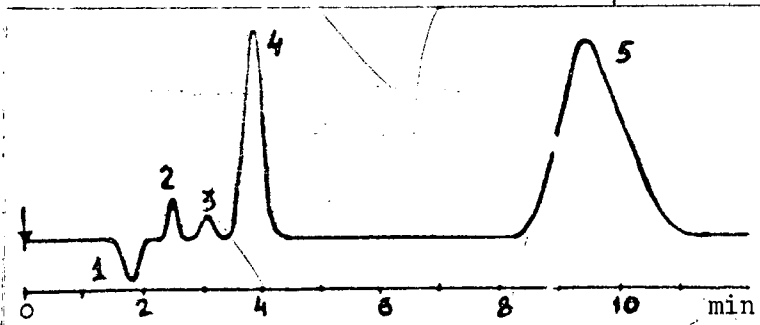


Figure 12.

NASA